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Charge-carrier mobilities in disordered semiconducting polymers: effects of carrier density and electric field

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We model charge transport in disordered semiconducting polymers by hopping of charge carriers on a square lattice of sites with Gaussian on-site energy disorder, using Fermi-Dirac statistics. From numerically exact solutions of the Master equation, we study the dependence of the charge-carrier mobility on temperature, carrier density, and electric field. Our results are used in calculating current-voltage characteristics of hole-only polymer diodes. It is found that very good fits to experimental current-voltage characteristics can be obtained at different temperatures, with reasonable fitting parameters for the width of the Gaussian density of states and the lattice constant. In agreement with the experiments we find that the density dependence is dominant over the field dependence. Only at high fields and low temperatures the field dependence becomes noticeable. The potential and current distribution show strong inhomogeneities, which may have important consequences for the operation of polymer opto-electronic devices.

1 Introduction

Charge conduction in semiconducting polymers is thought to take place by hopping of charge carriers in an energetically disordered landscape of hopping sites. In polymer field-effect transistors (FETs), where the number of carriers per site is rather high, charge-carrier mobilities show a strong dependence on the charge-carrier density, because of state-filling [1]. Mobilities in polymer light-emitting diodes (LEDs), where the number of carriers per site is very low, have up to now been assumed to have an important dependence, of the Poole-Frenkel form, on the electric field [2]. In order to explain such a dependence for a wide region of electric field strengths, the concept of correlated disorder was introduced [3] and different explanations have been proposed for this correlation [4-6]. In polymer diodes, however, it is hard to distinguish a field dependence of the mobility from a density dependence, since an increase of the electric field also leads to an increase of the number of injected carriers. Recently, it has been suggested that the previously assumed electric field dependence of the mobility in diodes of PPV-type polymers is, for a large part, actually a density dependence [7]. This suggestion has been supported by studies of current-voltage characteristics of hole-only diodes as a function of polymer layer thickness, which can be much better explained by assuming a density dependence than an electric field dependence [8]. Nevertheless, at low temperatures and high electric fields it still appears to be necessary to assume an electric

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field dependence, since a density dependence alone cannot explain all the current-voltage data [9]. In recent work [10], we were able to fit experimental current-voltage characteristics of hole-only polymer diodes of two different PPV-type polymers by using as input the results for the charge carrier mobilities obtained by solving the Master equation describing the hopping of charge carriers on a regular lattice of sites with Gaussian on-site energy disorder. Effects of state-filling and electric field on the mobility were taken into account. Interestingly, it was possible to obtain very good fits without invoking the complicating concept of correlated disorder. In the present work, we want to elaborate on these results and discuss a few new interesting results related to inhomogeneities in the potential and current distribution.

2 Method

We determine the charge-carrier mobility from a numerical solution of the Master equation obtained in the mean-field approximation for hopping of charge carriers on a lattice of sites:

$$\left[W_{ij}p_i\left(1-p_j\right)-W_{ji}p_j\left(1-p_i\right)\right]=0. \tag{1}$$

Here p_i is the time-averaged probability that site i is occupied by a charge and W_{ij} is the transition rate for hopping from site i to j. The factors $1 - p_i$ account for the fact that only one carrier can occupy a site, due to the high Coulomb penalty for the presence of two or more carriers. Assuming hopping of carriers from site to site by a thermally assisted tunnelling process and coupling to a system of acoustical phonons, we take, in line with earlier work, the transition rates of the form [11]:

$$W_{ij}=\begin{cases}\nu_0\exp\left[-2\alpha R_{ij}-\beta(\varepsilon_j-\varepsilon_i)\right], & \varepsilon_j\geq\varepsilon_i,\\ \nu_0\exp\left[-2\alpha R_{ij}\right], & \varepsilon_j<\varepsilon_i,\end{cases} \tag{2}$$

where $\beta \equiv 1/kT$, with T the temperature; ν_0 is an intrinsic rate, $R_{ij} \equiv |\mathbf{R}_j - \mathbf{R}_i|$ is the distance between sites i and j, α is the inverse localization length of the localized wave functions under consideration, and ε_i is the on-site energy of site i. The energy differences in Eq. (2) are supposed to contain a contribution $-eER_{ijx}$ due to an electric field E in the x-direction, where e is the charge of the carriers.

Equation (1) is solved by an iteration procedure similar to the one proposed in [6], starting from the zero-field Fermi-Dirac distribution. We take a regular cubic lattice with lattice constant a. For the inverse localization length we take $\alpha = 10/a$, a typical value for the polymers to which we apply our results [7]. Changing α predominantly changes the pre-factor of the resulting mobility, which is not a matter of concern here. We take into account hopping between nearest, next-nearest, and next-next-nearest neighbours, which is sufficient for this value of α. We focus on the parameter range where variable-range hopping, which sets in at very low temperatures [12], is not important. We draw the on-site energies randomly from a Gaussian distribution of width σ. Periodic boundary conditions are taken in all directions, reintroducing carriers leaving the lattice at the opposite side of the lattice, and the size of the lattice is taken large enough to avoid finite-size effects. The mobility is calculated as

$$\mu=\sum_{ij}W_{ij}p_i(1-p_j)R_{ij,x}/pEV, \tag{3}$$

with p the average carrier density and V the system volume. Averages are taken over a number of different disorder configurations such that μ is determined with an accuracy better than 10%.

3 Results and discussion

We display in Fig. 1 the calculated mobility as a function of carrier density, for a vanishing electric field, and as a function of electric field, for a low and a high density, typical for LEDs and FETs, respectively. The numerical results can be described rather well by the following parameterization scheme:

$$
\begin{aligned}
&\mu(T,p,E) \approx \mu(T,p) f(T,E),\\
&\mu(T,p) = \mu_0(T)\exp\left[\tfrac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2pa^3)^{\delta}\right],\\
&\mu_0(T) = \mu_0 c_1 \exp\left[-c_2\hat{\sigma}^2\right],\\
&\delta \equiv 2\frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)}{\hat{\sigma}^2}, \mu_0 \equiv \frac{a^2 \nu_0 e}{\sigma}, \hat{\sigma} \equiv \frac{\sigma}{kT},\\
&f(T,E) = \exp\left[0.44\left(\hat{\sigma}^{3/2} - 2.2\right)\left(\sqrt{1 + 0.8\left(\frac{Eea}{\sigma}\right)^2} - 1\right)\right]
\end{aligned}
\tag{4}
$$

with $c_1 = 1.8\cdot10^{-9}$ and $c_2 = 0.42$. The parameterization for the density dependence is based on a semi-analytical treatment of the problem, obtained as an extension of the analytical Vissenberg-Matters theory [1] for an exponential density of states to a Gaussian one [13]. The parameterization for the field dependence should be considered as purely empirical.

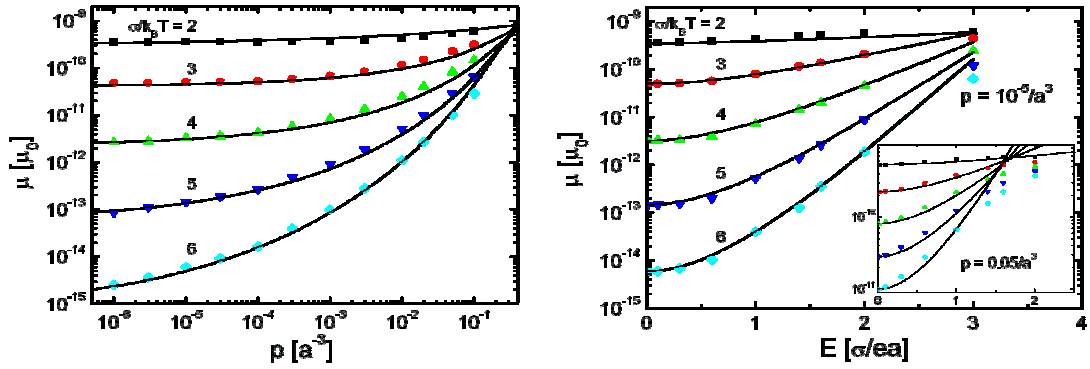

Fig. 1 Dependences of the mobility on the carrier density (left), for vanishing electric field, and on the electric field (right) for a low (main panel) and a high (inset) carrier density. Symbols: calculated results. Lines: Eq. (4).

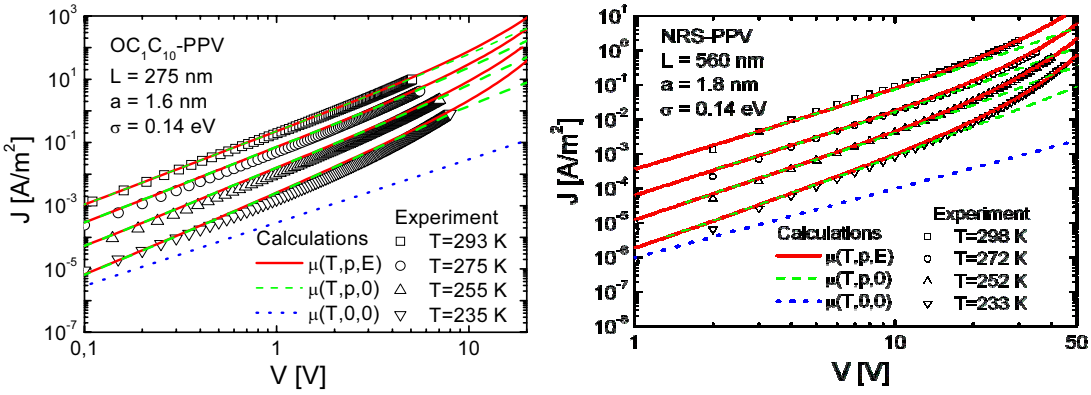

Fig. 2 Experimental (symbols) and calculated (lines) current density vs. voltage results for polymer hole-only diodes of two different PPV-type polymers, with polymer thickness L. Drawn lines: full dependence of the mobility on temperature (T), density (p) and field (E) taken into account. Dashed lines: only dependence on T and p taken into account. Dotted line: only dependence on T taken into account (displayed only for the lowest temperature).

In Fig. 2 we display fits of the current-voltage characteristics measured for two hole-only devices of PPV-type polymers to the current-voltage characteristics obtained with a mobility following from the parameterization Eq. (4), resulting from a space-charge limited current (SCLC) calculation [10]. The fits are very good, with reasonable values for the lattice constant a and the width of the Gaussian σ. Apart from the temperature dependence of the mobility, it turns out to be essential to take into account the density dependence. For the NRS-PPV device it is clear that it is also essential to take the field dependence at high voltages and low temperatures into account.

It is interesting to study the distribution of the electro-chemical potential and the current density following from the solution of Eq. (1). In Fig. 3 these are displayed in slices of the lattice for specific disorder configurations, at a moderately low carrier density. When the temperature decreases, "cliffs" start to appear where the potential has sudden jumps, separated by "terraces" on which the potential changes more gradually. Patches of very high current density appear on some of the terraces, avoiding the cliffs. These peculiar structures are expected to be important for the functioning of polymer opto-electronic devices, in particular in relation to exciton formation and local heating and degradation effects.

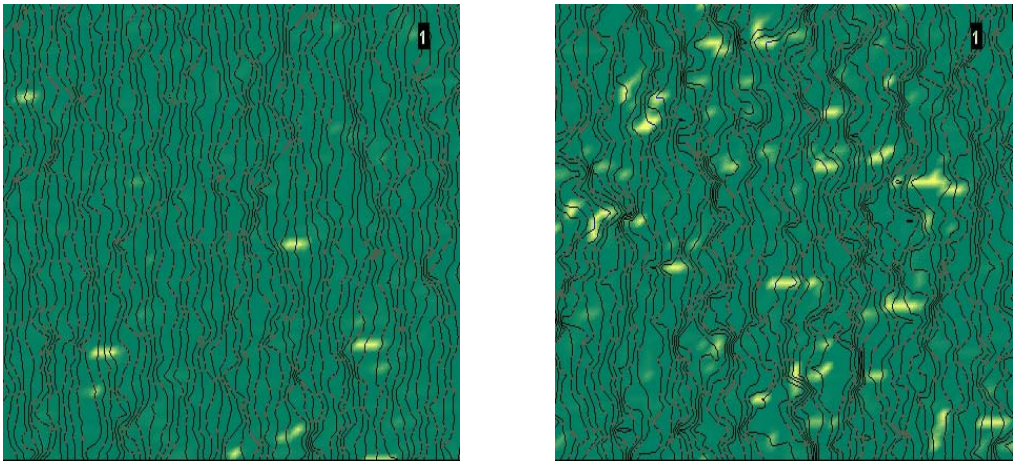

Fig. 3 Distribution of the potential and absolute value of the current density in a slice of a 60x60x60 array at a high (left figure, $\sigma/kT = 2$) and a low (right figure, $\sigma/kT = 6$) temperature, for a vanishing electric field. Sixty equipotential lines have been drawn and in the light regions the current density is more than 10x its average value. The carrier density is $p = 10^{-4}/a^3$. The electric field is oriented horizontally.

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